Radical Reactions

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Efficient Aerobic Oxidative Synthesis of 2-Substituted Benzoxazoles, Benzothiazoles, and Benzimidazoles Catalyzed by 4-Methoxy-TEMPO**

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Aerobic oxygenation/oxidation of hydrocarbons, alcohols, and amines catalyzed by aminoxyl radicals have been extensively studied.[1] However, its application in the catalytic oxidative synthesis of heterocycles is rare. Herein we report a novel and efficient aerobic approach for the synthesis of 2-substitued benzoxazoles, benzothiazoles, and benzimidazoles by using a one-pot reaction of aldehydes with 2-aminophenole, 2-aminothiophenol, and *o*-phenylenediamine, respectively, and an organic aminoxyl radical as the catalyst.

Five-membered heterocyclic rings, such as benzoxazoles, benzothiazoles, and benzimidazoles, are present in natural products, and in synthetic pharmaceutical and agrochemical compounds.[2] These compounds have been extensively studied for their biological and therapeutic activities, such as a cathepsin S inhibitor,[3] a HIV reverse transcriptase inhibitor,[4] an anticancer agent,[5] and an orexin-1 receptor antagonist.[6]

Classical methods for the synthesis of benzoxazoles involve two approaches. One is the copper-catalyzed intramolecular *ortho* arylation of *o*-haloanilides or the intermolecular domino annulations of *o*-arylhalides with acylamides.[7] The second approach is the condensation of 2-aminophenol with either carboxylic acid derivatives under strong acid/high temperature conditions,[8] or aldehydes with subsequent oxidation using strong oxidants such as 2,3-dichloro-5,6-dicyano-l,4-benzoquinone (DDQ),[9] $PhI(OAc)_2$,[10] $Th^{+}ClO_4^{-}$,[11] pyridiniumchlorochromate (PCC),[12] and $BaMnO_4$.[13] Recently, catalytic oxidative reactions using oxygen as the terminal oxidant have received much attention because of their green chemistry and atom economy aspects. The aerobic catalytic synthesis of benzoxazoles promoted by activated carbon[14] or copper nanoparticles[15] has recently been reported. However, these reactions require the use of large amounts of the catalyst (50 wt. % of special activated carbon) or excess base, and the yields were not satisfactory. Therefore, a more effective and environmentally friendly process is needed.

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[**] We are grateful to the National Natural Science Foundation of China (Grant No. 20472027) for financial support. We also thank Dr. Wei Yu for helpful discussions. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy free radical.

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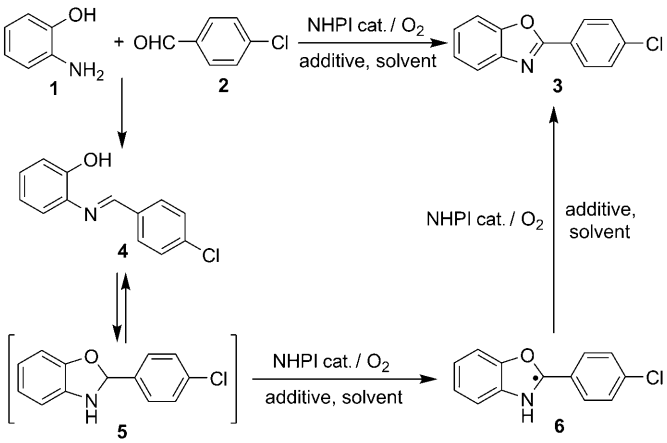
Recently, we reported an efficient approach to the oxidative dehydrogenation of Hantzsch dihydropyridines and pyrazolines using *N*-hydroxyphthalimide (NHPI) as the catalyst.[16] As an extension of this chemistry, we attempted to synthesize 2-aryl benzoxazoles **3** by the aerobic oxidation of Schiff base 2-(4-chlorobenzylideneamino)-phenol (**4**), which was obtained from the condensation of 2-aminophenol (**1**) and aldehyde **2**, using NHPI as the catalyst. The mechanism as shown in Scheme 1 was assumed to be operative.



Scheme 1. A proposed mechanism for the NHPI-catalyzed aerobic oxidative synthesis of 2-aryl benzoxazole.

We supposed that if benzoxazoline **5** was in equilibrium with imine **4**, the former could be easily oxidized to benzoxazole **3** by a hydrogen abstraction from the activated C–H bond of the benzoxazoline. This sequence could be initiated by a phthalimide-*N*-oxyl radical (PINO) generated in situ from the oxidation of NHPI by oxygen. Although several reaction conditions were tried to accomplish this reaction, only one gave target compound benzoxazole **3** albeit in unsatisfactory yield at high temperature using PhCN as the solvent (Table 1, entries 1–10). High temperature and PhCN as the solvent were needed because the cyclization of imine **4** to benzoxazoline **5** was difficult at low temperature. Notably, 4-chlorobenzaldehyde oxime was obtained as a product at relatively low temperature using CH_3CN as the solvent (Table 1, entries 3 and 4). To validate our proposal, *o*-phenylenediamine (**1e**) was used instead of 2-aminophenol (**1**) and the reaction was complete in acetonitile at 80 °C to give 2-(4-chlorophenyl)-1*H*-benzimidazole in 83 % yield. This yield results from the much higher nucleophilicity of the *ortho*-amine group compared to that of the *ortho*-hydroxy group for the cyclization to the imine.

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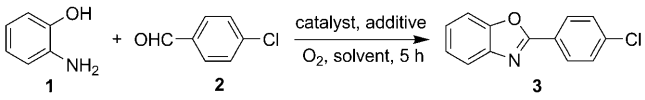
Table 1: Effect of aminoxyl radicals on the oxidative synthesis of 2-aryl benzoxazole.[a]

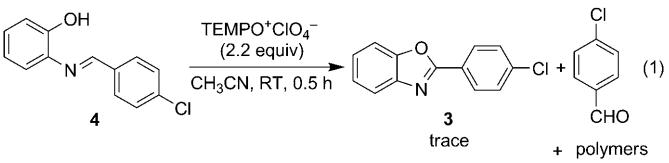


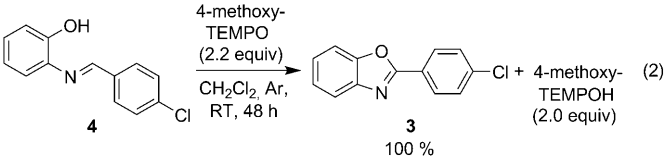
1 2 3

Entry	Catalyst [mol%]	Solvent	T [°C]	Yield [%][b]
1	NHPI (10)	CH_3CN	80	0
2[c]	NHPI/$Co(OAc)_2$ (10/0.5)	CH_3CN	RT	0
3	NHPI/$Co(OAc)_2$ (10/0.5)	CH_3CN	80	0[d]
4	NHPI (100)	CH_3CN	80	0[d]
5	NHPI (10)	$CH_3CO_2C_2H_5$	80	0
6	NHPI (10)	$CH_3CO_2C_4H_9$-*n*	120	0
7	NHPI (10)	CH_3CH_2OH	80	0
8	NHPI (10)	PhCN	120	trace
9	NHPI (10)	PhCN	150	15
10[e]	NHPI (10)	PhCN	150	71
11	TEMPO (5)	CH_3CN	80	18
12[c]	TEMPO/CuBr (5/0.5)	CH_3CN	RT	trace
13[c]	TEMPO/CuBr (10/1)	CH_3CN	RT	trace
14	TEMPO (5)	$CH_3CO_2C_2H_5$	80	13
15	TEMPO (5)	$CH_3CO_2C_4H_9$-*n*	120	23
16	TEMPO (10)	CH_3CH_2OH	80	15
17	TEMPO (5)	Benzene	80	21
18	TEMPO (5)	toluene	110	43
19[f]	TEMPO (10)	xylenes[g]	120	95
20	TEMPO (5)	xylenes[g]	120	95
21[e]	TEMPO (1)	xylenes[g]	120	96
22	TEMPO (5)	xylenes[g]	RT	5
23	0	xylenes[g]	120	0

[a] 2-aminophenol (**1**; 1 mmol) and aldehyde **2** (1 mmol) were dissolved in solvent (3 mL) in a 25 mL three-necked flask and stirred for 1 h at different temperatures. The catalyst was then added and the mixture stirred under an oxygen atmosphere for another 5 h. [b] ^{1}H NMR analysis. [c] Used 1 mol of Schiff base **4** as the substrate. [d] 4-Chlorobenzaldehyde oxime was obtained as the product. [e] After 15 h. [f] After 2.5 h. [g] Mixture of *o*-, *m*-, and *p*-xylene.

Next, we turned our attention to another aminoxyl radical, 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-methoxy-TEMPO) free radical, which is widely used for the selective oxidation of primary or secondary alcohols.[1c–d,17] We initially used stoichiometric amounts of $TEMPO^+ClO_4^-$ as the oxidant to perform this reaction. However, the starting material, 2-hydroxy-bezoimine **4**, was oxidatively decomposed to the corresponding aldehyde and 2-aminophenol (**1**); the strong oxidizing ability of $TEMPO^+$ caused the latter to be oxidized to give polymers, so only a trace amount of benzoxazole **3** was observed. However, when a stoichiometric amount of 4-methoxy-TEMPO radical was used as the oxidant instead of $TEMPO^+$, target molecule benzoxazole **3** was produced quantitatively in 48 hours at room temperature, indicating that 4-methoxy-TEMPO radical is a privileged oxidant in the oxidative dehydrogenation of Schiff base **4** [Eq. (1) and Eq. (2)].





4-methoxy-TEMPOH can be slowly oxidized to 4-methoxy-TEMPO radical in air at room temperature, so a strategy for the aerobic catalytic oxidative synthesis of benzoxazole using 4-methoxy-TEMPO radical as the catalyst was developed.

To optimize the reaction conditions we used various solvents and discovered that nonpolar aromatic solvents gave higher yields than polar solvents under the same reaction conditions; the solvent polarity affects the stability of the resonance structure of 4-methoxy-TEMPO radical and is also responsible for its reactivity with the substrate[18] (Table 1, entries 11, 14, 16, and 17). In addition, temperature significantly affected the reaction; high temperatures accelerated the rate of the hydrogen abstraction between 4-methoxy-TEMPO radical and the substrate, and the rate at which 4-methoxy-TEMPO radical was regenerated (Table 1, entries 17–19 and 22). Finally, we found that 4-methoxy-TEMPO/xylene catalytic system is best. All the conditions we optimized are listed in entries 11–23 in Table 1.

Notbaly, if 1 mol% of 4-methoxy-TEMPO was used, the reaction was complete in 15 hours, resulting in benzoxazole **3** in 96% yield. We checked the tunrover number (TON) and turnover frequency (TOF) values for different amounts of 4-methoxy-TEMPO radical (Table 2). The use of 1 mol% of 4-methoxy-TEMPO radical gave the best TON and TOF values.

The use of 5 mol% of 4-methoxy-TEMPO radical in the following reactions was aimed at reducing the reaction times. A variety of 2-aminophenol derivatives (**1a–1c**) and aldehydes **2** were used in this oxidative cyclization by the in situ formation of Schiff bases, leading to the synthesis of 2-substituted benzoxazoles (**3a–3o**; Table 3).

Aryl aldehydes gave excellent yields of 2-aryl benzoxazoles, and aliphatic aldehydes participated in the reaction to give the corresponding 2-alkyl benzoxazoles in good yields. When heptylaldehyde was used in the reaction, two benzoxazoles, **3i** and **3j**, were obtained in 20% and 35% yields, respectively (based on 2-aminophenol; Table 3, entry 9).We believe that 4-methoxy-TEMPO radical initially interacts with 2-hydroxybezoimine[19] and initiates the reaction with a hydrogen abstraction from the O–H bond of the phenol moiety[20] to produce phenoxyl radical **7** and 4-methoxy-

Table 2: TON and TOF values for 4-methoxy-TEMPO radical catalyzed oxidative synthesis of 2-aryl benzoxazole.[a]

Entry	4-methoxy-TEMPO [mol%]	t [h]	TON	TOF [h^{-1}]
1	10	2.5	10	4
2	5	5	20	4
3	1	15	100	6.7

[a] Calculated values based on Table 1, entries 19–21.

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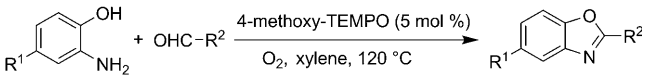
Table 3: 4-methoxy-TEMPO radical catalyzed aerobic oxidative synthesis of 2-substituted benzoxazoles.[a]

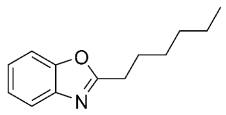


1a–1c **2** **3a–3o**

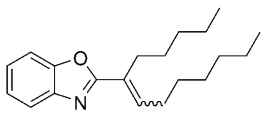
Entry	R^1	R^2	*t* [h]	Yield [%][b]
1	H (**1a**)	4-ClC_6H_4	5	95 (**3a**)
2	H (**1a**)	Ph	5	90 (**3b**)
3	H (**1a**)	4-$NO_2C_6H_4$	6	91[c] (**3c**)
4	H (**1a**)	2-$CH_3C_6H_4$	5	96 (**3d**)
5	H (**1a**)	4-$CH_3OC_6H_4$	4	95 (**3e**)
6	H (**1a**)	*E*-$C_6H_5CH{=}CH$	9	82 (**3f**)
7	H (**1a**)	2-furyl	8	88 (**3g**)
8	H (**1a**)	$(CH_3)_3C$	1	88 (**3h**)
9	H (**1a**)	$CH_3(CH_2)_5$	3	20, 35[d] (**3i,j**)
10	Cl (**1b**)	4-$CH_3OC_6H_4$	13	95 (**3k**)
11	Cl (**1b**)	4-$NO_2C_6H_4$	10	92[c] (**3l**)
12	NO_2 (**1c**)	2-$CH_3C_6H_4$	11	93[c] (**3m**)
13	NO_2 (**1c**)	4-ClC_6H_4	17	93[c] (**3n**)
14	NO_2 (**1c**)	$(CH_3)_3C$	6	91[c] (**3o**)

[a] 2-aminophenol (5 mmol) , aldehyde (5 mmol) and xylenes (15 mL; mixture of *o*-, *m*-, and *p*-xylene) was placed in a 100 mL three-necked flask and stirred at 120°C for 0.5 h. 4-methoxy-TEMPO radical (5 mol%; 47 mg, 0.25 mmol) was then added to the mixture and stirred for several hours under an oxygen atmosphere. [b] Yield of isolated product obtained after purificantion by silica gel column chromatography unless noted otherwise. [c] Yield of isolated product obtained after recrystallization. [d] Two compounds were obtained and structures are shown below.

TEMPOH which can be reoxidized to 4-methoxy-TEMPO radical by oxygen. Phenoxyl radical **7** is additionally stabilized



3i, minor

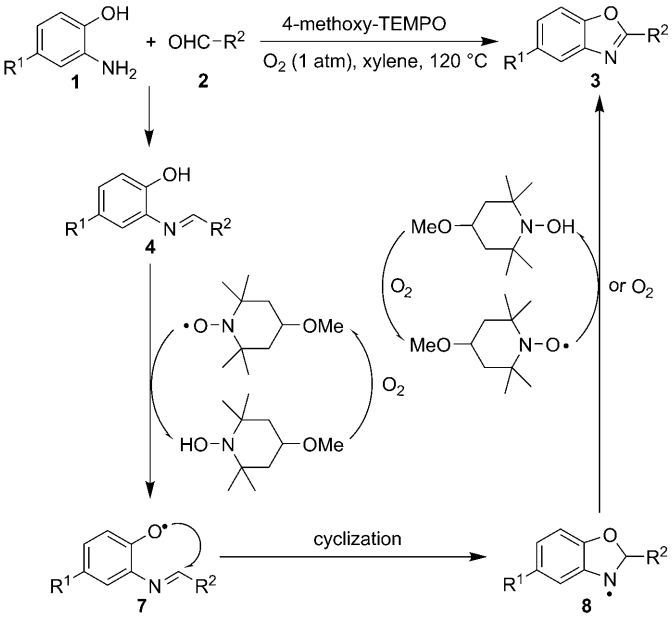


3j, major

by the imine moiety and then undergoes intramolecular 5-endo cycloaddition to the imine to form the corresponding aminyl radical **8**. The driving force for aromatization renders the second hydrogen abstraction, between the aminyl radical **8** and 4-methoxy-TEMPO/or oxygen, very effective and eventually yield target compound benzoxazole **3**. A proposed catalytic cycle is shown in Scheme 2.

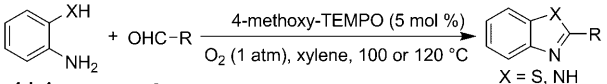
Having successfully achieved the aerobic oxidative synthesis of benzoxazoles, we expanded the catalytic system to the oxidative synthesis of benzothiazoles and benzimidazoles using 2-amino-thiophenol (**1d**) or *o*-phenylenediamine (**1e**) respectively with aldehydes as starting materials. As shown in Table 4, benzothiazoles and benzimidazoles were produced in high yields.

In conclusion, the reaction of 4-methoxy-TEMPO radical with 2-benzylideneaminophenols provides a novel and efficient approach for the aerobic catalytic oxidative synthesis of various heterocycles. The 2-substituted benzoxazoles, benzo-



Scheme 2. A proposed mechanism for 4-methoxy-TEMPO-catalyzed aerobic oxidative synthesis of 2-substituted benzoxazoles.

Table 4: 4-methoxy-TEMPO radical catalyzed aerobic oxidative synthesis of 2-substituted benzothiazoles and benzimidazoles.[a]



1d–1e **2** **3p–3w**

Entry	X	R	*t* [h]	Yield [%][b]
1	S (**1d**)	Ph	9	80 (**3p**)
2	S (**1d**)	4-ClC_6H_4	11	85 (**3q**)
3	S (**1d**)	4-$NO_2C_6H_4$	7	87[d] (**3r**)
4	S (**1d**)	$(CH_3)_3C$	3	77 (**3s**)
5[c]	NH (**1e**)	Ph	11	91[d] (**3t**)
6[c]	NH (**1e**)	4-ClC_6H_4	10	91[d] (**3u**)
7[c]	NH (**1e**)	4-$CH_3OC_6H_4$	7	89[d] (**3v**)
8[c]	NH (**1e**)	2-Furyl	13	90[d] (**3w**)

[a] 2-aminothiophenol or *o*-phenylenediamine (5 mmol), aldehydes (5 mmol), and xylenes (15 mL; mixture of *o*-, *m*-, and *p*-xylene) was placed in a 100 mL three–necked flask and stirred at 100°C for 0.5 h. 4-methoxy-TEMPO radical (5 mol%; 47 mg, 0.25 mmol) was added to the mixture which was then stirred for several hours under an oxygen atmosphere.[b] Yield of isolated product after purification by silica gel column chromatography unless noted otherwise.[c] At 120°C.[d] Yield of isolated product obtained by recrystallization.

thiazoles, and benzimidazoles can be obtained by using a one-pot reaction of aldehydes with 2-aminophenole, 2-amonothiophenol and *o*-phenylenediamine, respectively, with 4-methoxy-TEMPO radical as the catalyst. The extension of this catalytic system for the preparation of other useful heterocycles is underway in our laboratory.

Experimental Section

Aerobic synthesis of benzoxazole **3a** (Table 3, entry 1): 2-aminophenol (546 mg, 5 mmol) and 4-chlorobenzaldehyde (703 mg,

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5 mmol) were placed in a 100 mL three-necked flask containing xylenes (15 mL; mixture of *m*-, *o*-, and *p*-xylene). The reaction mixture was heated to 120 °C for 0.5 h with stirring. 4-methoxy-TEMPO (47 mg, 5 mol %) was then added to the mixture which was then stirred under an oxygen atmosphere for 5 h. When the starting materials were completely consumed as determined by TLC analysis, the reaction mixture was concentrated under vacuum and the product was isolated after purification using silica gel column chromatography as a white crystalline solid (1.100 g ; 95 %). The identity and purity of the product was confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis.

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[1] For reviews, see: a) Y. Ishii, S. Sakaguchi, T. Iwahama, *Adv. Synth. Catal.* **2001**, *343*, 393 – 427; b) F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800 – 3842; c) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051 – 1071; d) R. A. Sheldon, I. W. C. E Arends, G.-J. Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774 – 781; e) C. Galli, P. Gentili, O. Lanzalunga, *Angew. Chem.* **2008**, *120*, 4868 – 4874; *Angew. Chem. Int. Ed.* **2008**, *47*, 4790 – 4796; f) T. Vogler, A. Studer, *Synthesis* **2008**, 1979 – 1993; g) J. Piera, Jan-E. Bäckvall, *Angew. Chem.* **2008**, *120*, 3558 – 3576; *Angew. Chem. Int. Ed.* **2008**, *47*, 3506 – 3523.

[2] For examples in medicinal chemistry, see: a) M. L. McKee, S. M. Kerwin, *Bioorg. Med. Chem.* **2008**, *16*, 1775 – 1783; b) E. Oksuzoglu, O. Temiz-Arpaci, B. Tekiner-Gulbas, H. Eroglu, G. Sen, S. Alper, I. Yildiz, N. Diril, E. Aki-Sener, I. Yalcin, *Med. Chem. Res.* **2008**, *16*, 1 – 14; c) S.-T. Huang, I.-J. Hsei, C. Chen, *Bioorg. Med. Chem.* **2006**, *14*, 6106 – 6119; d) C. G. Mortimer, G. Wells, J.-P. Crochard, E. L. Stone, T. D. Bradshaw, M. F. G. Stevens, A. D. Westwell, *J. Med. Chem.* **2006**, *49*, 179 – 185; e) M. C. Van Zandt, M. L. Jones, D. E. Gunn, L. S. Geraci, J. H. Jones, D. R. Sawicki, J. Sredy, J. L. Jacot, A. T. DiCioccio, T. Petrova, A. Mitschler, A. D. Podjarny, *J. Med. Chem.* **2005**, *48*, 3141 – 3152; f) M. Hranjec, M. Kralj, I. Piantanida, M. Sedic, L. Suman, K. Pavelic, G. Karminski-Zamola, *J. Med. Chem.* **2007**, *50*, 5696 – 5711; g) M. L. Morningstar, T. Roth, D. W. Farnsworth, M. Kroeger Smith, K. Watson, R. W. Buckheit, Jr., K. Das, W. Zhang, E. Arnold, J. G. Julias, S. H. Hughes, C. J. Michejda, *J. Med. Chem.* **2007**, *50*, 4003 – 4015.

[3] D. C. Tully, H. Liu, P. B. Alper, A. K. Chatterjee, R. Epple, M. J. Roberts, J. A. Williams, K. T. Nguyen, D. H. Woodmansee, C. Tumanut, J. Li, G. Spraggon, J. Chang, T. Tuntland, J. L. Harris, D. S. Karanewsky, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1975 – 1980.

[4] J. A. Grobler, G. Dornadula, M. R. Rice, A. L. Simcoe, D. J. Hazuda, M. D. Miller, *J. Biol. Chem.* **2007**, *282*, 8005 – 8010.

[5] J. Easmon, G. Pürstinger, K.-S. Thies, G. Heinisch, J. Hofmann, *J. Med. Chem.* **2006**, *49*, 6343 – 6350.

[6] K. Rasmussen, M.-A. Hsu, Y. Yang, *Neuropsychopharmacology* **2007**, *32*, 786 – 792.

[7] a) R. D. Viirre, G. Evindar, R. A. Batey, *J. Org. Chem.* **2008**, *73*, 3452 – 3459; b) G. Evindar R. A. Batey, *J. Org. Chem.* **2006**, *71*, 1802 – 1808; c) G. Altenhoff, F. Glorius, *Adv. Synth. Catal.* **2004**, *346*, 1661 – 1664.

[8] M. Terashima, M. Ishii, Y. Kanaoka, *Synthesis* **1982**, 484 – 485.

[9] J. Chang, K. Zhao, S. Pan, *Tetrahedron Lett.* **2002**, *43*, 951 – 954.

[10] R. S. Varma, R. K. Saini, O. Prakash, *Tetrahedron Lett.* **1997**, *38*, 2621 – 2622.

[11] K. H. Park, K. Jun, S. R. Shin, S. W. Oh, *Tetrahedron Lett.* **1996**, *37*, 8869 – 8870.

[12] C. Praveen, K. H. Kumar, D. Muralidharan, P. T. Perumal, *Tetrahedron* **2008**, *64*, 2369 – 2374.

[13] R. G. Srivastava, P. S. Venkataramani, *Synth. Commun.* **1988**, *18*, 1537 – 1544.

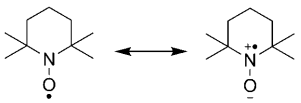
[14] Y. Kawashita, N. Nakamichi, H. Kawabata, M. Hayashi, *Org. Lett.* **2003**, *5*, 3713 – 3715.

[15] M. Kidwai, V. Bansal, A Saxena, S. Aerryb, S. Mozumdar, *Tetrahedron Lett.* **2006**, *47*, 8049 – 8053.

[16] a) B. Han, Q. Liu, Z.-G. Liu, R.-Z. Mu, W. Zhang, Z.-L. Liu, W. Yu, *Synlett* **2005**, 2333 – 2334; b) B. Han, Z.-G. Liu, Q. Liu, L. Yang, Z.-L. Liu, W. Yu, *Tetrahedron* **2006**, *62*, 2492 – 2496.

[17] a) X. Wang, R. Liu, Y. Jin, X. Liang, *Chem. Eur. J.* **2008**, *14*, 2679 – 2685; b) R. Liu, X. Liang, C. Dong, X. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 4112 – 4113.

[18] It is well known that two kinds of resonance structures for TEMPO exist (**I** and **II**). The structures result from the unpaired electron delocalized between the nitrogen and the oxygen atoms. The greater the solvent polarity, the more favored structure **II** will be, as it has the larger electron density on the oxygen atom and spin density on the nitrogen atom. Structure **II** should reduce the hydrogen abstraction reactivity of TEMPO with phenols. Otherwise, the hydrogen-bonding interaction of TEMPO with protic solvents should disturb the interaction between TEMPO and phenols. See: a) P. Franchi, M. Marco Lucarini, P. Pedrielli, G. F. Pedulli, *ChemPhysChem* **2002**, *3*, 789 – 793, and references therein; b) L. R. C. Barclay, C. E. Edwards, M. R. Vinqvist, *J. Am. Chem. Soc.* **1999**, *121*, 6226 – 6231.



I **II**

[19] The intermolecular hydrogen-bonding interaction between TEMPO and phenol has been studied both in solution and solid state. For solution studies, see: a) I. G. Shenderovich, Z. Kecki, I. Wawer, G. S. Denisov, *Spectrosc. Lett.* **1997**, *30*, 1515 – 1523; for solid-state studies the single crystal structure of TEMPO·phenol adduct was obtained, see: b) B. Ahrens, M. G. Davidson, V. T. Forsyth, M. F. Mahon, A. L. Johnson, S. A. Mason, R. D. Price, P. R. Raithby, *J. Am. Chem. Soc.* **2001**, *123*, 9164 – 9165.

[20] For the hydrogen absraction between TEMPO and phenols, see: a) C. Aliaga, A. Aspée, J. C. Scaiano, *Org. Lett.* **2003**, *5*, 4145 – 4148; b) C. Aliaga, J. M. Jua'rez-Ruiz, J. C. Scaiano, A. Aspée, *Org. Lett.* **2008**, *10*, 2147 – 2150.

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